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New halogenated flame retardants in the atmosphere of nine urban areas in China: Pollution characteristics, source analysis and variation trends[☆]

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ABSTRACT

Since the ban of polybrominated diphenyl ethers (PBDEs) excluding deca-BDE in China, new halogenated flame retardants (NHFRs), such as new brominated flame retardants and Dechlorane Plus, have become widely used. In this study, we assessed the atmospheric gaseous and particulate levels of eight NHFRs in nine urban areas in China. We detected high mean atmospheric (vapour plus particle phases) concentrations of tetrabromophthalate (TBPH) (74.8 pg m^{-3}) and decabromodiphenyl ethane (DBDPE) (68.8 pg m^{-3}), two major NHFRs. Most of the gaseous and particulate NHFR concentrations presented seasonal variations (from summer to autumn), possibly driven by temperature. Spatially, concentrations and patterns of the NHFRs differed among the nine cities. Significantly higher concentrations were detected in cities with higher gross domestic products. The composition, especially the DBDPE/TBPH ratio (S), were clearly different among the cities, which pattern in each city are likely driven by variations in the type of industries operating in each city. Based on the temporal analysis of other researches and our data, PBDE levels have decreased markedly, while NHFRs levels have increased. Since high NHFR levels had detrimental effects on public health, NHFRs research warrants more attention.

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1. Introduction

Flame retardants are a class of chemicals that have been widely used in construction materials (e.g. furniture and electronics) to reduce the likelihood of ignition for human safety since the 1960s (Stapleton et al., 2014). Before their ban, polybrominated diphenyl ethers (PBDEs) was a widely used type of flame retardant. With the discovery of their bioaccumulation tendency and potential toxicity, many studies were undertaken to assess their pollution characteristics, sources, and exposure to humans. Since the ban of the commercial production of penta- and octa-BDEs (Ma et al., 2013; Yang et al., 2013), PBDE levels in Chinese cities have progressively decreased (Lin et al., 2016). Chlorinated and brominated flame retardants, the most common types of flame retardants, have

attracted attention in recent years, because several of these compounds have been detected widely in the environment and bodies of organisms (Chen et al., 2011). New brominated flame retardants (NBFRs), including bis(2-ethylhexyl) tetrabromophthalate (TBPH), 2-ethylhexyl tetrabromobenzoate (TBB), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy) ethane (TBE), and decabromodiphenyl ethane (DBDPE), are used extensively as replacements for PBDEs. TBPH is usually used in combination with TBB at an approximate ratio of 1:4 to impede fire burning (Stapleton et al., 2008). They are used mainly in the insulative material of wires, cables, carpets, wall decorations and adhesives. Meanwhile, DBDPE contributes to 50% of the total concentration of NBFRs in dust samples in China (Qi et al., 2014b). It is used as a flame retardant, mainly in computers, TVs, phones, etc (Table S1). (Zheng, 2015) Several studies have detected NBFRs in the environment and biota (Baron et al., 2014; Cequier et al., 2015; Ali et al., 2013; Ali et al., 2014). Dechlorane Plus (DP) (*syn*- and *anti*-isomers), a new chlorinated flame retardant, is typically used in wires, cable coatings and hard plastic connectors. It has been

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detected in ambient air, fish and sediment samples (Hoh et al., 2006). Several NHFRs have a tendency to bioaccumulate and are potentially toxic (Ezechias et al., 2014). In addition, there is evidence that some NHFRs, including TBB and TBPH, have the potential for long-range atmospheric transportation (Ma et al., 2012).

Following trends in economic development, numerous types of products containing NHFRs have been produced (e.g. electronics, clothing and furniture). Moreover, the annual growth rate of flame retardant production in China was recently reported to be ~15% (Yu et al., 2016). The production of DP reached 2000 t in Jiang Su Province, China in 2006 (Covaci et al., 2011). No detailed information is available on the production of TBPH in China; however, production in the United States increased from 450 to 4500 t/yr between 1990 and 2006. In China, the production of DBDPE has increased by 80% per year since 2006, reaching 12,000 t (Qi et al., 2014b). Moreover, 600 t HBB are produced annually in Qingdao, Shandong Province, China (Covaci et al., 2011).

Flame retardants have attracted the attention of researchers in recent years, and an increasing number of institutional and academic groups are participating in research on flame retardants in China. However, little of this research has been focused on new flame retardants, and existing studies on NHFRs have targeted mainly those found in soil, surface water and sediments (He et al., 2012; Chen et al., 2013; Zheng et al., 2015). Regardless, the number of studies on NHFRs in the atmosphere is increasing. Several studies have been performed in urban areas (Qi et al., 2014a; Liu et al., 2016a), because cities have denser populations, greater industrial activity and higher levels of consumption than those of remote areas. In addition, atmospheric NHFRs in cities can exert greater harm more readily because of the dense populations, and NHFRs can readily migrate into neighbouring regions via atmospheric transport. Therefore, it is essential to investigate NHFRs in different types of cities throughout China.

In this study, we collected eight NHFRs from nine cities across China in summer and autumn. These areas are distributed from the eastern seaboard to the western interior, representing different geographical locations in China. All compounds were detected in vapour and particle phases to determine their pollution characteristics and to identify potential sources of NHFRs in China.

2. Materials and methods

2.1. Sample collection

We selected nine urban sites (Fig. 1) in eastern coastal and western interior China to measure atmospheric NHFRs concentrations. These cities can be divided into two groups according to population (Table S2): megalopolises (Beijing, Tianjin and Guangzhou) and large/medium cities (Qingdao, Xiamen, Kunming, Mianyang and Nanchang). All sampling sites were located on the top floor of buildings on university campuses or research institutes, with no obvious obstructions around them. All samples were collected in the summer (June 17–August 24) and autumn (September 2–October 20) of 2014.

The vapour and particle samples were collected using high-volume active air samplers (Tisch Environmental, Inc., Cleves, OH, USA) (for sampling information, see Table S2). Fibreglass membranes (Whatman, USA) with a pore size of 0.7 μm were used to collect the particle samples, which were calcined in a muffle furnace at 450 $^{\circ}\text{C}$ for 8 h. The vapour samples were collected in polyurethane foam (PUF; $d = 6.5$ cm, $h = 7.5$ cm, $\rho = 0.030$ g cm^{-3}). The PUF was pretreated with dichloromethane (DCM) and acetone via Soxhlet extraction for 48 h before collecting the samples, and the PUF was sealed after vacuum drying. At the end of each sampling period, the fibreglass membranes and PUF were wrapped in

clean foil paper and stored at -20 $^{\circ}\text{C}$ until chemical analysis.

2.2. Sample pretreatment

Each sample was spiked with 20 ng surrogate recovery standards (PCB 209 and PCB 198) and extracted with DCM for 36 h using Soxhlet. Each sample was condensed using a concentration evaporator and solvent-exchanged in n-hexane. An alumina/silica column (i.d. = 8 mm) was used to clean the extracts. The column was packed from bottom to top with neutral alumina (1 g, 3% deactivated), neutral silica gel (3 g, 3% deactivated), 50% sulphuric acid silica gel (3 g) and anhydrous sodium sulphate (1 g). Under a gentle stream of nitrogen, each NHFRs sample was concentrated to a total volume of 0.5 mL by eluting the liquid extract, which was composed of hexane and DCM (V:V, 1:1). Finally, a gel permeation chromatography column was used to clean the samples. Then, 55 mL hexane/DCM (V:V, 1:1) were used to load and elute the concentrated samples. The first 15 mL of the fraction were discarded, and the following 40 mL containing the NHFRs and recovery standard were collected. Then, 30 μL n-octane, containing 10 ng ^{13}C -PCB 141 as an internal standard, were added as a keeper. Finally, all samples were concentrated to a volume of 30 μL under a gentle nitrogen stream and stored at -20 $^{\circ}\text{C}$ until injection.

2.3. Instrumental analysis

We performed gas chromatography coupled with electron capture negative ion mass spectrometry (Agilent GC7890 coupled with 5975C MSD) using a DB5-MS capillary column (15 m \times 0.25 mm i.d. \times 0.25 μm film thickness) to measure *anti*- and *syn*-DP and six NBFRs (TBPH, PBEB, HBB, TBB, TBE and DBDPE). Helium was used as carrier gas to carry the extracts, and methane was used as the chemical ionisation moderating gas. The temperature of the ion source was maintained at 230 $^{\circ}\text{C}$, and that of the transfer line was 280 $^{\circ}\text{C}$. The temperature of the gas chromatography oven was held at 110 $^{\circ}\text{C}$ for 1 min, increased to 200 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ and held for 1 min, and finally raised to 310 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$ and held for 12 min. PBEB, HBB, TBE and DBDPE were monitored at mass to charge ratios (m/z) of 78 and 81. TBB was monitored at an m/z of 357, TBPH was monitored at m/z of 462 and 464, and *syn*- and *anti*-DP were monitored at an m/z of 653.8.

2.4. Quality assurance/control

We included a procedural blank, a field blank for every site in each season (vapour and particle phases) and a duplicated sample for every 10 samples to test for potential contamination and repeatability. All compounds were not found in blank samples. The instrument and method detection limit ranges were 0.10–0.36 pg and 0.015–0.18 pg m^{-3} , respectively (more detailed information in S1). The standard spiked recoveries were 78.1–111%, and all results were not corrected based on the surrogate recoveries. The detailed information of statistical analysis was performed in S2.

3. Results and discussion

3.1. Concentrations and compositions

Most of the eight measured NHFRs were detected in both the vapour and particle phases in all nine Chinese cities (Table 1). Unlike PBDEs, which are detected predominantly in the vapour phase (Yang et al., 2013), except decabromodiphenyl ether (BDE-209), most NHFRs including DP and DBDPE were detected at higher concentrations in the particle phase. The mean atmospheric

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